



DYE REMOVAL FROM TEXTILE WASTEWATER BY CHITOSAN GUARGUM BASED HYDROGELS

¹Vrinda J, ²Bindu G

¹Post Graduate student, ²Associate Professor

¹Department of Civil Engineering,

¹Government Engineering College, Thrissur, India

Abstract: Textile wastewater is nowadays a major source of surface water contaminations, where different technologies have been applied for treatment of these carcinogenic effluents. Among the dyes, vat dyes are insoluble in water and are highly stable compared to other dyes. They are used for colouring cellulosic fiber specially cotton fiber. Removal of this vat dye can be a challenging process. Due to the unique physical and chemical characteristics of hydrogels, such as hydrophilicity, swellability and modifiability, there is increasing research interest in the development and application of novel hydrogels in water and wastewater treatment. Hydrogels have exhibited superior performance in the adsorptive removal of a wide range of aqueous pollutants including heavy metals, nutrients, and toxic dyes. Chitosan and guar gum are among the world's most abundant and low-cost biopolymers that is natural, renewable, environmentally benign, cost-efficient, nontoxic, biodegradable, and biocompatible. Chitosan guar gum based hydrogels were found to be very effective in the removal of Vat Orange 3G dye. The effect of various parameters such as pH and contact time on the adsorption process by the hydrogel was studied with synthetic wastewater. The effect of pH was studied initially by batch experiments and found that better efficiency in dye removal was at a lower pH of 4. The study on effect of time showed an increase in percentage removal with increase in time and reached a maximum value of 85% within 2 hrs. From the adsorption kinetics study it was found that the adsorption process by the chitosan guar gum hydrogel followed pseudo second order kinetics. Thus chitosan guar gum based hydrogels is a promising technology in the removal of vat dye which is an ecofriendly method.

Index Terms - Chitosan, Guar gum, Hydrogels, Adsorption.

I. INTRODUCTION

Dyes which are complex organic compounds even in low concentration can reduce photosynthetic activities in aquatic fauna by preventing the penetration of light and oxygen. The heavy metals and dyes discharged into the aquatic systems are non-biodegradable, cannot be metabolized and get accumulated in the body which results in various mutagenic, carcinogenic effects, allergies, skin irritation and heart defects in the living organisms. Numerous traditional methods like adsorption, chemical precipitation, flocculation coagulation, membrane filtration, ultra-filtration, electro dialysis, microbial degradation, photocatalysis, reverse osmosis and ion exchanger method have been used to remove heavy metals and poisonous dyes from the wastewater. Dyes are difficult to decolourise due to its complex structure and synthetic origin. Among the treatment technologies, adsorption is an attractive and viable option, provided that the sorbent is inexpensive and readily available for use. Adsorption has been considered as one of the most efficient methods, because of its relatively fast reaction, flexibility, simplicity of design, ease of operation, comparatively low cost, norelease of harmful secondary pollutants, availability of wide range of adsorbents etc. Adsorption of dyes is a process of attracting dye molecules to the surface of a solid adsorbent and fixing them through physical or chemical bonds. Some of the widely used adsorbents were activated carbon, zeolite, modified porous silica, bamboo dust, peat, lignite, fungi, moss, bark husk, chitin, coir pith, maize cob, pinewood, sawdust, rice husk, sago waste etc. Even though activated carbon-based adsorption technology is still used for treatment of wastewater, it is not cost- and energy-efficient. Alternatively, the application of biopolymers such as chitosan and guar gum are the emerging adsorption methods for the treatment of textile effluents containing dyes and heavy metal ions, even at low concentrations. Chitosan is one of the world's most abundant and low-cost biopolymers that is natural, renewable, environmentally benign, cost-efficient, nontoxic, biodegradable, and biocompatible. Guar gum polysaccharides are also nontoxic, low cost and renewable raw material that can be potentially used for high performance applications. Hydrogels are the three-dimensional network structures having high-molecular weight, and composed of polymeric chains along with crosslinking agent, which do not normally dissolve in water at physiological temperature and pH, but swell due to water absorption. Hydrogels with high sorption capacity, high functionality and hydrophilicity pave a probable way for decolourisation of organic dye pollution, as being cost effective, high on demand, biodegradable and their ease of preparation. Cross-linking the resultant blend of chitosan and guar gum forms a highly porous and stable hydrogel. Thus Chitosan-Guar gum (CS-GG) based hydrogel can be used as a cost effective and environment friendly material for dye removal.

Objectives of the study

- To remove Vat Orange 3G dye from wastewater.
- To find the efficiency of chitosan guar gum based hydrogel in removing Vat orange 3G dye.
- To find the effect of various parameters on the efficiency of removal of the dye

II. MATERIALS AND METHODS

2.1 Materials

Chitosan

Chitosan, a deacetylated derivative of chitin, is a linear cationic biopolymer of glucosamine residues. It is made by treating the chitin shells of shrimp and other crustaceans with an alkaline substance, like sodium hydroxide. Chitosan was used in preparation of hydrogel and its different modified forms were used for wastewater treatment in many studies. Chitosan of degree of deacetylation 90.0 % was used for the study.

Guargum

Guargum, a polysaccharide composed of the sugars galactose and mannose extracted from guar beans. It has thickening and stabilizing properties that are useful in the food, feed and industrial applications. Guargum powder of 99% purity was used for the study.

Vat Orange 3G dye

Vat Orange 3G ($C_{42}H_{23}N_3O_6$) dye was used for the dye removal studies. Its molecular weight is 665.65 g/mol, density is 1.537 and color is orange red.

2.2 Methods

2.2.1 Fabrication of chitosan guargum hydrogels

Chitosan and Guargum are the main ingredients in the fabrication of the hydrogels. Guar gum solution of 0.6%(w/v) final concentration and chitosan solution of 1.4%(w/v) final concentration were mixed by stirring with a magnetic stirrer at 40°C for 60 min and were crosslinked with Glutaraldehyde (0.001%), 0.007% glycerol was added as a plasticizer and crossed linked the solution for 3 hrs. The final mixture was poured into moulds and incubated at 40 °C overnight. Next morning the gels were removed from the moulds and stored in sealed bags at room temperature for further use (Sami et al., 2017). The preparation of the solutions of chitosan and guargum (Rithe et al., 2014) are described below.

Preparation of Chitosan Solution

In a beaker 1.4g of chitosan was added to 100ml of 2%(v/v) acetic acid solution. The mixture was stirred for 4 h at room temperature, at 150 rpm. Chitosan is insoluble in plain distilled water, but is readily soluble in acidic solution.

Preparation of Guargum Solution

In a beaker 0.6g of guargum was added to 100ml of distilled water and was kept under mechanical stirring for 48 hrs at 150 rpm. A couple of drops of 98% concentrated sulphuric acid were then added to this solution and was mechanically stirred for another 1 h at an rpm of 150 at room temperature. The solutions of guargum and chitosan prepared were mixed in the ratio 1: 2.34 (Sami et al., 2017).

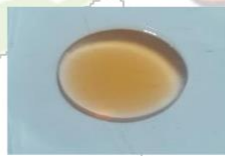


Fig 1. Fabricated Chitosan Guargum based hydrogel

2.2.2 Evaluation of dye removal

In this study, synthetic dye wastewater each of 100 ml, of concentration of 80 mg/L was taken in beaker and treated with chitosan guargum based hydrogel with adsorbent dosage of 260 mg/L for a contact time of about 2 hrs. The contact time was fixed as 2 hrs based on previous studies where chitosan and guargum hydrogels achieved equilibrium within 2 hrs in adsorption of anionic dyes at an initial dye concentration of 100 mg/L. The adsorbent dosage was fixed as 260 mg/L as the chitosan guargum based hydrogel showed an optimum adsorption of anionic structures in an acidic environment (Sami et al., 2017). The samples with the adsorbents were continuously stirred in an orbit shaker at 100 rpm and at 25°C and the solution was finally filtered through whatman filter paper and the dye concentration of remaining solution was measured using UV-Vis spectrophotometer at 440 nm. The percentage dye removal and amount of dye adsorbed are determined by Eqn 2.1 and Eqn 2.2 respectively.

$$\text{Percentage Dye Removal, } R (\%) = \frac{C_i - C_e}{C_i} \times 100 \quad (2.1)$$

$$\text{Amount of dye adsorbed, } q (\text{mg/g}) = \frac{M}{V} \quad (2.2)$$

Where C_i - Initial dye concentration (mg/l), C_e - Equilibrium dye concentration (mg/l), V - Volume of dye solution (l) and M -Mass of adsorbent (g).

2.2.3 Adsorption kinetics

Adsorption kinetics is a curve (or line) that describes the rate of retention or release of a solute from an aqueous environment to solid-phase interface at a given adsorbent dosage, temperature, flow rate and pH. In other words, it is the measure of adsorption uptake with respect to time. During adsorption two main processes are involved; physical (physisorption) or chemical (chemisorption). Physical adsorption is as a result of weak forces of attraction (van der waals), while chemisorption involves the formation of a strong bond between the solute and the adsorbent that involves the transfer of electrons. To depict the adsorption kinetics of the adsorbent two conventional kinetic models, pseudo-first order and pseudosecond order models are applied to the experimental results.

Pseudo-first order kinetics

The linear form of pseudo-first order model was depicted in Eqn 2.3.

$$\log (q_e - q_t) = \log q_e - (K_1 \cdot t)$$

Pseudo-Second Order Model

The linear form of pseudo-second order model was depicted in Eqn 2.4.

$$t/q_t = \frac{1}{K_2 q_e^2} + \frac{t}{q_e}$$

(2.3)

(2.4)

q_e - Adsorbed amount of dye (mg/g) at an equilibrium time

q_t - Adsorbed amount of dye (mg/g) at a designated time, t (min)

K_1 and K_2 - Rate constants for the pseudo-first-order and pseudo-second order model (1/min)

III. RESULTS AND DISCUSSION

3.1 Results Of Adsorption Studies

3.1.1 Effect of pH

The pH is considered to be one of the most important factors affecting the adsorption process, as pH can influence not only the surface charge of the adsorbent, but also the chemistry of dye solution. The electrostatic interactions between the adsorbent and the adsorbate are predominantly dictated by the pH of the media due to the fluctuations in charge differentials on both the adsorbate and the surface of the adsorbent. The chitosan guar gum based hydrogel showed maximum swelling in the lower pH range of 4 to 6. At acidic pH, the amount of H^+ in the medium is higher which aids the swelling of the hydrogel. At neutral pH, both the free NH_2 groups and OH groups of guar gum have decreased interaction with protons due to unavailability of protons, so the swelling capacity decreases. Subsequently, at basic pH, the ionization degree of the charged species decreases, moreover the degree of protonation of NH_2 group also decreases thus resulting in minimal water absorption and low swelling at pH 10. That is more positively charged surfaces are obtained at lower pH values and this favours the uptake of electron rich dye molecules which are negatively charged. Thus maximum dye removal is obtained at pH 4 as shown in Table 1. The dye concentration of the synthetic wastewater sample was 80mg/L. The contact time was fixed as 2 hrs based on previous studies where chitosan hydrogels and guar gum hydrogels achieved equilibrium within 2 hrs in adsorption of anionic dyes at an initial dye concentration of 100 mg/L. The adsorbent dosage was fixed as 260 mg/L as the chitosan guar gum based hydrogel showed an optimum adsorption of anionic structures in an acidic environment (Sami et al., 2017).

Table 1. Effect of pH on Dye Removal (Adsorbent Dosage=260 mg/L, Initial Dye Concentration=80 mg/L, Contact time=2 hrs)

pH	C_e (mg/L)	R (%)
4	12.45	84.43
5	13.52	83.10
6	13.85	82.68
7	14.56	81.80

3.1.2 Effect of Contact Time

The effect of contact time on percentage removal of dye by chitosan guar gum based hydrogels are shown in Table 2. It was observed that the dye removal process comes to a constant within 2 hrs and the removal efficiency was found to be around 85%.

Table 2. Effect of Contact Time on Dye Removal (Adsorbent Dosage=260mg/L, Initial Dye Concentration=80 mg/L, pH=4)

Contact Time (min)	C_e (mg/L)	R (%)
30	33.45	58.18
60	22.01	72.48
90	11.88	85.15
120	11.72	85.35

3.3 Adsorption Kinetics

The adsorption kinetics of the chitosan guar gum based hydrogel on removal of vat orange 3G dye was studied based on the batch observation studies. Fig 2. and Fig 3. depicts the pseudo first order and pseudo second order models for chitosan guar gum based hydrogels. The dye adsorption studies showed that it is a time dependent process

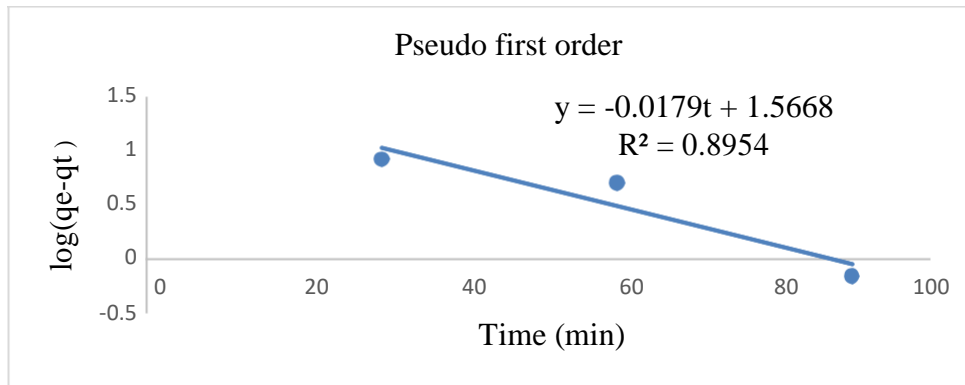


Fig 2. Pseudo first order kinetic model for Chitosan Guar gum based hydrogels

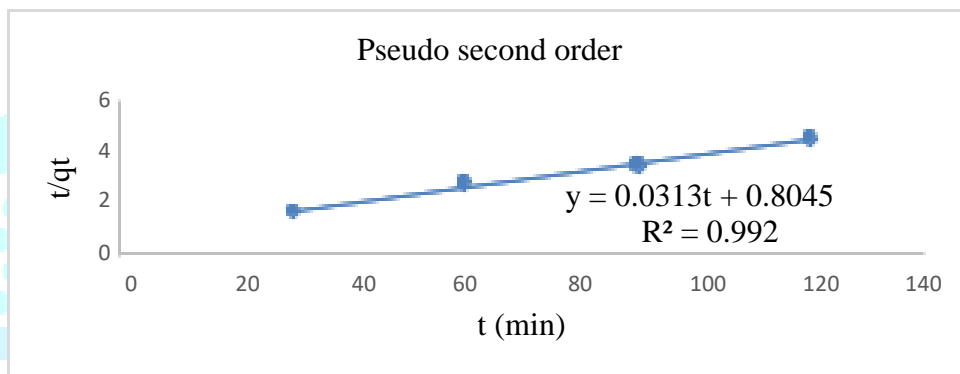


Fig 3. Pseudo second order kinetic model for Chitosan Guar gum based hydrogels

Table 3. Pseudo first order kinetic model parameters for Chitosan Guar gum based hydrogels

Equation	K_1	R^2
$\log(q_e - q_t) = -0.0179t + 1.5668$	0.04122	0.8954

Table 4. Pseudo second order kinetic model parameters for Chitosan Guar gum based hydrogels

Equation	K_2	R^2
$t/q_t = 0.0313t + 0.8045$	0.07208	0.992

According to Table 3 and Table 4 pseudo second order model's regression coefficient was better than that for the pseudo first order model since the R^2 (0.992) is greater.

IV. CONCLUSIONS

This study investigated the performance of Chitosan Guar gum based hydrogel in the removal of Vat Orange 3G dye. It was found to be very effective in the removal of Vat Orange 3G dye. The effect of various parameters such as pH and contact time on the adsorption process by the hydrogel was studied with synthetic wastewater. The effect of pH was studied initially by batch experiments and found that better efficiency in dye removal was at a lower pH of 4. The study on effect of time showed an increase in percentage removal with increase in time and reached a maximum value of 85% within 2 hrs. From the adsorption kinetics study it was found that the adsorption process by the chitosan guar gum hydrogel followed pseudo second order kinetics. It can be concluded that chitosan guar gum based hydrogels is a promising technology in the removal of vat dye which is an ecofriendly method.

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